REMOVAL OF MALACHITE GREEN FROM AQUEOUS SOLUTION BY USING DRIED WATER HYACINTH *(Eichhornia Crassipes)*

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ABSTRACT

This paper shows a detailed study to investigate the potential of water hyacinth as adsorbent, to remove Malachite Green from aqueous solution and to identify the optimum condition for the parameter involved. There were four parameters that have been studied in this paper, they were effect of adsorbent dosage, effect of initial concentration of dye, effect of pH and effect of time contact. It was found that the optimum dosage for the adsorbent at initial dye concentration of 60 mg/L was 0.6 g, the optimum pH was at 6 and the optimum time contact was at 60 minutes for initial concentration 60 mg/L. At the optimum condition the removal of malachite green was increased as the initial concentration was increased. The optimum adsorption of malachite green was occurred at pH basic because the pH dependence of dye uptake could be related to functional group of the adsorbent and also to solution chemistry. The dye uptakes were analyzed by using UV-Vis Spectrometer. The result proved that dried water hyacinth is a good adsorbent to remove malachite green from waste water because it is economically feasible and high efficiency of dye removal from dilute solutions and also applicable for industrial.

ABSTRAK

Kajian ini dilakukan untuk mengkaji keupayaan keladi bunting sebagai penjerap untuk menyingkirkan Malachite Green dari larutan akuas dan untuk mengenalpasti keadaan optimum bagi faktor penghad yang terlibat. Terdapat empat faktor penghad yang telah dikaji iaitu kesan dos penjerap, kesan kepekatan awal, kesan pH dan kesan masa bersentuhan. Telah didapati bahawa dos yang optimum bagi penjerap pada kepekatan awal 60 mg/L ialah 0.6g, keadaan yang optimum bagi pH ialah pada pH 6 dan masa yang optimum ialah pada 60 minit untuk kepekatan awal 60 mg/L. Pada keadaan yang optimum penyingkiran Malachite Green meningkat apabila kepekatan awal meningkat.Penjerapan untuk Malachite Green berlaku pada pH alkali kerana kebergantungan pH untuk menyingkirkan adalah berkait dengan kumpulan berfungsi penjerap dan juga dengan larutan kimia. Hasil kajian membuktikan bahawa serbuk keladi bunting adalah penjerap yang baik untuk menyingkirkan Malachite Green dari air buangan kerana efektif dari segi ekonomi dan kecekapan penyingkiran pewarna yang tinggi dari larutan cair dan juga boleh digunakan untuk industri.

TABLE OF CONTENT

LIST OF ABBREVIATION

MG	Malachite Green
WH	Water Hyacinth
DWH	Dried Water Hyacinth
FTIR	Fourier transform infra red
HCL	Hydrochloric Acid
NaOH	Sodium Hydroxide
rpm	Revolution per minutes
Ppm	part per million
LCAs	low cost adsorbents
mg/L	milligrams per liter
DM/ha	dry matter per hectare
q_e	uptake capacity
µ	Micro
g	Gram
L	Liter
m	Meter
^0C	Degree Celcius

LIST OF TABLES

LIST OF FIGURES

LIST OF APPENDIX

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Many industries such as textile, leather tanning, paper and pulp, and food consume dyes extensively (M.Hasnain Isa *et al*., 2007). The presence of dyes and pigments in water, even at very low concentrations, is highly visible and undesirable. It not only affects an esthetic merit, but also inhibits sunlight penetration and reduces photosynthetic action within ecosystem (Wen Cheng *et al*., 2008).The dye under consideration is Malachite Green (MG), which is important water-soluble dye belonging to triphynelmethane family. MG is widely used to dye wool, silk, cotton, and leather materials. In agriculture, commercial fish hatchery and animal husbandry also acts as an antifungal therapeutic agent, while for human it is used as antiseptic and fungicidal.

Most of the dyes, including malachite green, are toxic and must be removed before discharge into receiving streams. Research has indicated that MG can be toxic to human cells and promotes liver tumor formation. This dye may enter into the food chain and could possibly cause carcinogenic, mutagenic and teratogenic (Wen Cheng *et al*., 2008). MG has a complicated chemical structure it is resilient to fading on exposure to light and water. Therefore, MG is difficult to be removed from wastewaters by commonly used techniques. However, since it dissociates in aqueous solutions, it is prone to be strongly adsorbed into adsorbent such as dried water hyacinth (DWH).

There are various physical-chemical processes have been extensively used in effective treatment of the dye-containing wastewater. For example, most effective method to remove the dyes is adsorption on activated carbons which has been proven in removing dyes from aqueous solution. However, activated carbon is still considered expensive and currently the research is focused on the low-cost adsorbents for this purpose (K.Vasantha Kumar *et al*., 2005).This process becomes economic if the adsorbent is inexpensive and does not require any expensive pretreatment. The use of biomaterials as adsorbents for the treatment of wastewaters will provide a potential alternate to the conventional treatment. Adsorption processes are being employed widely for large-scale in environmental recovery and purification applications (Mi-Hwa Baek *et al*., 2009). As a consequence, considerable researches are recently being devoted to study the removal of dyes from aqueous solution using adsorption, chemical and also biological degradation methods.

In the present investigation,water hyacinth (*Eichhornia Crassipes*) was used as adsorption and evaluated to remove the MG dye. The water hyacinth (WH) is a free floating aquatic weed originated in Amazon in South America where it was kept under control by natural predators (Carina C.Gunnarsson *et al*., 2007). It is found abundantly throughout the year in very large and drainage channel system and around the fields of irrigation. WH also has been listed as the most troublesome weed in aquatics systems. Recently, this plant has received attention because of its potential to remove pollutants such as heavy metals and dyes. The objective of this study was to evaluate the ability using WH for adsorption to remove MG including the effect of different parameters including adsorbent dosage, initial concentration of MG, contact time and pH of solution.

1.2 Problem Statement

Dye pollutants from various industries are an important source of environmental contaminations. Most industries use dyes and pigments to colour their products. Perhaps dyes are the serious polluters of our environment as far as colour pollution is concerned. The effluents from dye manufacturing and consuming industries are highly coloured coupled with high BOD, COD and suspended solids. The dyes are generally stable to light, oxidizing agents, heat and their presence in wastewaters offers considerable resistance to their biodegradation, and thus upsetting aquatic life. Colour affects the nature of water and inhibits the sunlight penetration into the stream and reduces photosynthetic activity. Some of the dyes are carcinogenic and mutagenic (Oaulid Hamdaoui *et al.*, 2008).

Most commercial treatment systems use activated carbon as adsorbent to remove dyes in wastewater because it has excellent adsorption ability. But its widespread use is limited due to high running cost. Many low-cost adsorbents, including natural materials waste materials from industry and agriculture have been proposed by several researches. These materials do not require any expensive additional pretreatment step and could be used as adsorbents for removal of dyes from solution (Runping Hun *et al.*, 2007). In this study, water hyacinth is chosen as adsorbent to remove the malachite green because according to K.S.Low *et al.*, 1995 the ability of WH to remove heavy metals in solution is well documented. This means that the root system could act as an adsorption medium for various materials which are soluble in water. As well known, MG is a water-soluble dye that commonly used nowadays.

Several researchers reported, water hyacinth grows and reproduces in a very high rate and is considered the worst aquatic plant. The characteristic of water hyacinth float on the water surface, blocking navigation and interfere with irrigation, fishing, recreation, and power generation. It is also prevent sunlight penetration and reduce the aeration of water, leading to oxygen deficiency, competitively exclude submerged plants, and reduce biological diversity (Mohammad I. El-Khaiary *et al*., 2007). Many researches have been conducted in efforts to create a use for dumped water hyacinth. This includes research on biogas generation fish feed and animal feed. In this study the waste WH, was used and evaluated as a possible adsorption for the removal of a cationic dye which is MG from aqueous solution.

In this study, dried water hyacinth (DWH) is chosen because it is environmental friendly which cannot lead to growth of mosquitoes' pest and not affect the spread of dengue fever to the residents nearby. It is also can prevent the bad odors. Another advantages using the DWH because this adsorbent easy to store and handling. Furthermore, we can reduce the space of transportation and the cost to transport itself as to commercialize this work. Based on the previous study, WH will be the good adsorbents chosen in adsorption of MG in industrial wastewater.

1.3 Objective

The objective of this study is to remove the Malachite Green from aqueous solution by using the dried water hyacinth (DWH).

1.4 Scope of Study

In order to achieve the objectives, the following scopes have been identified:

i. Effect of dried water hyacinth dosage.
ii. Effect of initial concentration.
iii. Effect of pH of solution.
iv. Effect of time.

1.3 Rationale And Significance

The purpose of this study is to remove malachite green which causes environmental and health problem because MG has complex structure that cannot be degraded or destroyed. It can cause dangerous because it can enter our bodies via food chain. In this study, we use dried water hyacinth (DWH) because there is evidence that, the weed of this plant has attracted worldwide attention due to its fast spread and congested growth.

By doing this study, we can also helps to improve the environment problems that caused by water hyacinth such as the blockage of canals and rivers that can even cause dangerous flooding. Besides that, water hyacinth is a low-cost, high efficiency of metal removal from dilute solutions and easily available material for adsorbent (Kaustubha Mohanty *et al*., 2005). Moreover, using DWH have many advantages such as to prevent the dengue fever cause by aquatic WH and also can cut the cost of the commercialize process. WH also as a low cost adsorbent and high efficiency of removal dye in aqueous solution.

CHAPTER 2

LITERATURE REVIEW

2.1 Adsorption

2.1.1 Definition

Adsorption is a process in which atoms or molecules move from a bulk phase that is solid, liquid, or gas onto a solid or liquid surface. Adsorption is to be distinguished from absorption, a process in which atoms or molecules move into the bulk of a porous material, such as the absorption of water by a sponge. The term adsorption is most often used in the context of solid surfaces in contact with liquids and gases.

In simple terms, adsorption is the collection of a substance onto the surface of adsorbent solids. It is a removal process where certain particles are bound to an adsorbent particle surface by either chemical or physical attraction. Refer to Mohammad I.El-Khaiary *et al*., 2007; adsorption is widely used to remove pollutants from waste water. Adsorption of dyes from wastewater has been studied before to find a suitable explanation of the mechanism and the kinetics.

Adsorption is one of the processes, which besides being widely used for dye removal also has wide applicability in waste water treatment. The term adsorption refers to a process wherein a material is concentrated at a solid surface from its liquid or gaseous surroundings. Figure 2.1, show that the attraction mechanism of adsorption process on to the medium with the present of positive and negative charge.

Gas phase adsorption is a condensation process where the adsorption forces condense the molecules from the bulk phase within the pores of adsorbent. The driving force for adsorption is the ratio of the partial pressure and the vapour pressure of the compound. The adsorption capacity for non-polar organics increases with the boiling point, molecular weight and concentration of the air contaminant. Low molecular weight (less than 50) and highly polar compounds such as formaldehyde, methane, and ethanol will not be ready adsorbed at low concentration. Liquid phase adsorption, the molecules go from the bulk phase to being adsorbed in the pores in semi-liquid state. The driving force for adsorption is the ratio of the concentration to the solubility of the compound.

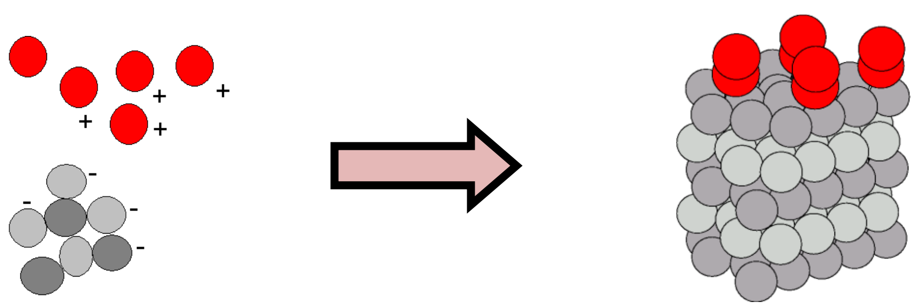

Figure 2.1: The Adsorption process.

2.1.2 Adsorbent

An adsorbent is a substance, usually porous in nature and with a high surface area that can adsorb substance onto its surface by intermolecular without changing the adsorbent physically or chemically. The most widely used adsorbent is activated carbon and usually prepared from coal, coconut shell, lignite and wood. However, this adsorbent is limited because it is expensive and hard to regenerate. Many researched have been done to produce the cheaper adsorbent to replace costly wastewater treatment methods such as chemical precipitation, ion exchange, electroflotation membrane separation, reverse osmosis, electrodialysis, solvent extraction and many others. Adsorption of low cost adsorbent is one of the physic-chemical treatment processes found to be effective in removing dyes in aqueous solution. According to Bailey *et al*., (1999) an adsorbent can be considered as cheap or low- cost adsorbent if it is abundant in nature, requires little processing and a by-product of waste materials from waste industry.

Only at very low concentrations the adsorption isotherm linear, at higher concentrations the adsorption isotherm may be Langmuir or Freundlich in nature. Due to the fact that solutes can distribute between the adsorbent surface and a mobile phase, adsorbents are used as a stationary phases in gas-solid and liquid-solid chromatography. Adsorbents are also used for extraction purposes removing traces of organic materials from large volumes of water very efficiently. Typical adsorbents used in gas-solid chromatography are silica gel, alumina, carbon and bonded phases. These are mostly used in the separation of the permanent gases and the low molecular weight hydrocarbon gasses. Adsorbents used in liquid solid chromatography are mostly silica gel and various types of bonded phases. Adsorbents in liquid-solid chromatography have a very wide variety of application areas.

A review of the low cost adsorbent was well documented in the journal of Gupta *et al*., 2009.

Table 2.1: List of LCAs intensively decolorizing synthetic dyes (Gupta *et al*., 2009)

Species	**Adsorbent**	**References**
Malachite Green	Oil palm trunk fiber	Hameed and El-Khaiary *et al*., (2008)
	AC-groundnut shell	Malik *et al*., (2007)
	AC from pine sawdust	Akmil-Basar *et al*., (2005)
	Sawdust carbon	Garg *et al*., (2003)
	Neem sawdust, Sugarcane dust	Khattri *et al*., (1999) and Singh *et al*.,(2000)
Acid blue 25	Saw dust-pitch pine	Ferrero *et al*., (2007)
	Cane (bagasse) pith	Juang *et al*., (2001)
	Water Hyacinth	Lee *et al*., (1999)
Acid red 14	Soy meal hull	Arami *et al*., (2006)
	Banana peel	Annadurai *et al*., (2002)
	Orange peel	Annadurai *et al*., (2002)
Acid yellow 36	Rice husk carbon	Malik *et al*., (2003)
Methylene Blue	Fallen pheonix's tree leaves	Runphing Han *et al*., (2007)
	Jackfruit (Artocarpus heteropyllus) leaf powder	Md. Tamez Uddin *et al*., (2009)
	Biosolid	M. Sarioglu *et al*., 2006
Phenol	Water hyacinth ash	M. T. Uddin et al., 2007
Lead, Cadmium, Zinc, and Copper	Carbon developed from walnut, hazelnut, almond, pistachio shell, and apricot.	Maryam Kazemipour *et al*., 2007

2.1.3 Adsorption Process

In the few years, many researchers have been done to prove that the kinetics studies have been very helpful to determine the process of adsorption. There is several equation of kinetics for adsorption can be used. It is showed that the results and graph plotted are almost all precise, undesirable and always can be interpreted easily. The most important for adsorption process to determine the mechanism of sorption for the design purpose. Generally, the adsorption dynamics is accepted to consist of the three consecutive steps:

i. Transport of adsorbate molecules from the bulk solution to the adsorbent external surface through the boundary layer diffusion.
ii. Diffusion of the adsorbate from the external surface into the pore of the adsorbent.
iii. Adsorption of the adsorbate on the active sites on the internal surface of the pores.

As the general, adsorbability of a compound increased with the increasing molecular weight, a higher number of functional groups such as double bonds or halogen compounds and also increasing polarisability of the molecule. There are many studies conducted, proven that the boundary layer diffusion is the rate controlling steps in the system by dilute concentration of adsorbate,poor mixing, and small particle size of adsorbent. In addition, the interparticle diffusion controls the rate of adsorption in system by high concentrations of adsorbate, vigorious mixing and large particle size of adsorbent.

Usually, the layer diffusion is dominant at the beginning of adsorption during the initial removal, and then the rate of adsorption is regularly controlled by the intraparticle diffusion as the capacity of adsorbate has loaded the external surface of adsorbent. From the last step, adsorption is very rapid to be compare with the first two steps. For that reason, it can be considered that the overall rate of adsorption is controlled by either the boundary layer or pore diffusion, or combining both.

Based on the previous study, the amount of dye adsorbed at time t, q_t was calculated from the mass balance equation (Q. Sun, L. Yang *et al.*, 2003):

$$q_t = \frac{(C_0 - C_t)V}{m} \quad 2.1$$

Where q_t is the amount of MG adsorbed (mg/g) at time,C_0 is the initial dye concentration in liquid phase (mg/L),C_t represents the liquid phase dye concentration at equilibrium (mg/L), V is the volume of dye solution used (L) and m is the mass of adsorbent used(g).

2.2 Water Hyacinth

The water hyacinth (*Eichhornia crassipes*) is a free-floating aquatic plant, which over the past century, has been spread around the world by human (Gopal *et al.*, 1987). Outside its native range is South America it can quickly grow to very high densities over 60 kg/m^2, thereby completely clogging water bodies. It has been listed as most troublesome weed in aquatic systems. When uncontrolled, the relatively high growth rate of this plant and the robustness of its seeds can disturb the aquatic ecosystem equilibrium, inducing environmental damages. It is a severe environmental and economical problem in many tropical and subtropical parts of the world. It forms dense mats that prevent river traffic, block irrigation canals.

As water hyacinth decays, there is a sharp increase in nutrient levels in water body, which ultimately creates the problem of eutrophication in aquatic system. Other effects of the fast growth are physical interference with fishing, obstruction of shipping